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To cite this article: S Nizamoglu *et al* 2007 *Nanotechnology* **18** 065709

Nanotechnology **18** (2007) 065709 (5pp) doi:10.1088/0957-4484/18/6/065709

White light generation using CdSe/ZnS core–shell nanocrystals hybridized with InGaN/GaN light emitting diodes

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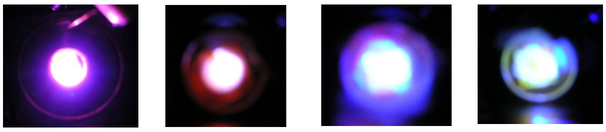
Received 31 October 2006, in final form 28 November 2006
Published 10 January 2007
Online at stacks.iop.org/Nano/18/065709

Abstract
We introduce white light generation using CdSe/ZnS core–shell nanocrystals of single, dual, triple and quadruple combinations hybridized with InGaN/GaN LEDs. Such hybridization of different nanocrystal combinations provides the ability to conveniently adjust white light parameters including the tristimulus coordinates (x, y), correlated colour temperature (T_c) and colour rending index (R_a). We present the design, growth, fabrication and characterization of our white hybrid nanocrystal-LEDs that incorporate combinations of (1) yellow nanocrystals ($\lambda_{PL} = 580$ nm) on a blue LED ($\lambda_{EL} = 440$ nm) with $(x, y) = (0.37, 0.25)$, $T_c = 2692$ K and $R_a = 14.69$; (2) cyan and red nanocrystals ($\lambda_{PL} = 500$ and 620 nm) on a blue LED ($\lambda_{EL} = 440$ nm) with $(x, y) = (0.37, 0.28)$, $T_c = 3246$ K and $R_a = 19.65$; (3) green, yellow and red nanocrystals ($\lambda_{PL} = 540$, 580 and 620 nm) on a blue LED ($\lambda_{EL} = 452$ nm) with $(x, y) = (0.30, 0.28)$, $T_c = 7521$ K and $R_a = 40.95$; and (4) cyan, green, yellow and red nanocrystals ($\lambda_{PL} = 500$, 540, 580 and 620 nm) on a blue LED ($\lambda_{EL} = 452$ nm) with $(x, y) = (0.24, 0.33)$, $T_c = 11\,171$ K and $R_a = 71.07$. These hybrid white light sources hold promise for future lighting and display applications with their highly adjustable properties.

Lighting poses an increasing market demand as one of the next great solid-state frontiers [1]. For that, white light emitting diodes (WLEDs) have attracted both scientific attention and commercial interest with their potential wide-scale use, for example, in architectural lighting, decorative lighting, flashlights and backlighting of large displays [2]. To date, multi-chip WLEDs, monolithic WLEDs and colour-conversion WLEDs, commonly with yellow phosphorus, have been extensively exploited [3–5]. Also, as an alternative approach, nanocrystals (NCs) have recently been used for colour conversion in white light generation; a blue/green two-wavelength InGaN/GaN LED coated with a single type of red NC and a blue InGaN/GaN LED with a single type of yellow NC and a dual type with red and green NCs have been reported [6–9].

In the most common approach of colour-conversion WLEDs coated with phosphorus, although phosphorus is good for photoluminescence across the visible, its emission spectrum is fixed. On the other hand, the use of combinations of nanocrystals provides the ability to adjust the white light parameters. To this end, in this work for the first time, we present white light generation with adjustable parameters using multiple combinations of NCs, each of which features a narrow emission spectrum widely tunable across the visible spectral range. Hybridizing CdSe/ZnS core–shell NCs of various single, dual, triple and quadruple combinations with InGaN/GaN LEDs, we demonstrate white light generation with adjustable tristimulus coordinates, correlated colour temperature and colour rending index. Here we present the design, epitaxial growth, fabrication and characterization of



(a) (b) (c) (d)

Figure 1. Photographs of our white hybrid NC-WLEDs while emitting white light: (a) yellow NCs (λ_{PL} = 580 nm) hybridized with blue LED (λ_{EL} = 440 nm), (b) cyan and red NCs (λ_{PL} = 500 and 620 nm) with blue LED (λ_{EL} = 440 nm), (c) green, yellow and red NCs (λ_{PL} = 540, 580 and 620 nm) with blue LED (λ_{EL} = 452 nm), and (d) cyan, green, yellow and red NCs (λ_{PL} = 500, 540, 580 and 620 nm) with blue LED (λ_{EL} = 452 nm).

our hybrid NC-WLEDs as shown in figure 1 while generating white light. With this proof-of-concept demonstration, we observe that it is possible to use nanocrystal hybridization on display units to tune their colour parameters as is required in specific commercial applications.

The operating principle of these hybrid NC-WLEDs relies on the hybrid use of the LED as the pump light source and the integrated NC film as the photoluminescent layer. When electrically driven, the LED optically pumps the NCs. The photoluminescence of these NCs and the electroluminescence of the LED consequently contribute together to the white light generation. Here, with the ability to tune the NC photoluminescence peaks across the visible (using the size effect) and with the right choice of NC combinations, we cover the visible spectrum from blue to red with a necessary spectral power distribution. Furthermore, with the small overlap between the NC emission and absorption spectra, we conveniently modify the white light spectrum as desired with the addition of NCs.

To adjust the optical properties of the generated white light, we carefully set the device parameters including the type and density of NCs and the thickness and order of the NC films. The type of NCs determines the intervals of the visible spectrum designed to contribute to white light. The NC density and the film thickness affect the level of conversion from incident photons to emitted/transmitted photons for each NC layer. The order of NC films, with a different NC type in each film, sets the level of reabsorption of the photons emitted by the preceding NC layers. Therefore, the ability to control such hybrid device parameters makes it possible to generate the intended white light spectrum.

We use four types of CdSe/ZnS core–shell NCs with their photoluminescence in the visible spectral range of cyan, green, yellow and red. The NC diameters and their corresponding peak photoluminescence wavelengths are provided in table 1. We use these NCs blended in host resin with a size distribution of ±5%. We use NC film thickness ranging from 400 to 1700 μm and NC density ranging from 3.04 to 140 nanomoles per 1 ml of resin.

We use two types of blue InGaN/GaN LEDs, one with a peak electroluminescence at 440 nm and the other at 452 nm. We use an epitaxial layer design identical for both of the blue LEDs with the only change being the epitaxial growth temperatures of their respective active layers. The design of these InGaN/GaN LEDs is presented along with the thickness of each epitaxial layer in figure 2.

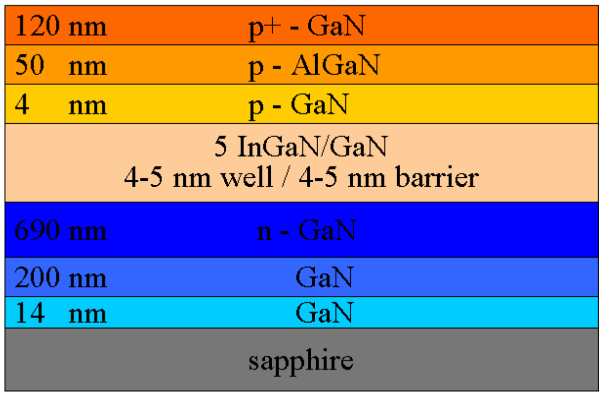


Figure 2. Epitaxial structure of our blue LEDs (not drawn to scale).

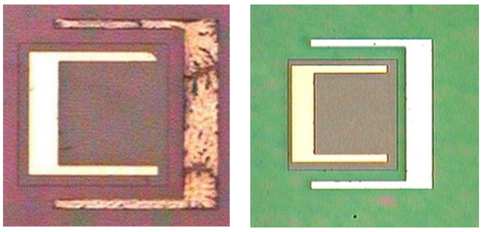
Table 1. Size of our nanocrystals.

Nanocrystal photoluminescence colour	Crystal diameter (nm)	Peak emission wavelength (λ_{PL}) (nm)
Cyan	1.9	500
Green	2.4	540
Yellow	3.2	580
Red	5.2	620

We use a GaN dedicated metal organic chemical vapour deposition (MOCVD) system (Aixtron RF200/4 RF-S) for the growth of our epitaxial layers at Bilkent University Nanotechnology Research Center. We start with a 14 nm thick GaN nucleation layer and a 200 nm thick GaN buffer layer to increase the crystal quality of the device epitaxial layers. Subsequently, we grow a 690 nm thick, Si doped n-type contact layer. We then continue with the epi-growth of five 4–5 nm thick InGaN wells and GaN barriers as the active layers of our LEDs. The growth temperature of this active region determines the amount of In incorporation into the wells, which in turn adjusts the emission peak wavelength. Therefore, we use distinct active region growth temperatures for the two types of our LEDs: one at 682 °C for 440 nm EL peak and the other at 661 °C for 452 nm EL peak. Finally, we finish our growth with p-type layers that consist of Mg-doped, 4 nm thick p-GaN, 50 nm thick $Al_{0.1}Ga_{0.9}N$ and 120 nm thick GaN layers as the contact cap. Following the growth, we activate Mg dopants at 750 °C for 15 min.

In the device fabrication, we use standard semiconductor processing including photolithography, thermal evaporator (metallization), reactive ion etch (RIE) and rapid thermal annealing. Our p-contacts consist of Ni/Au (15 nm/100 nm) and are annealed at 700 °C for 30 s under N_2 purge. On the other hand, our n-contacts consist of Ti/Al (100 nm/2500 nm) and are annealed at 600 °C for 1 min under N_2 purge. Top-view micrographs of two of our fabricated blue LEDs (with λ_{EL} = 440 nm in (a) and λ_{EL} = 452 nm in (b)) are shown in figure 3. For on-chip integration, following the surface treatment, we hybridize the LED top surface with various types of NCs in a UV-curable host polymer. We cure the coated samples for 1 h under the UV lamp for each film.

Our cyan, green, yellow and red NCs exhibit photoluminescence (PL) peaks at 500, 540, 580 and 620 nm, respectively,



(a) (b)

Figure 3. Micrographs of our fabricated blue LEDs: (a) with $\lambda_{EL} = 440$ nm and (b) with $\lambda_{EL} = 452$ nm.

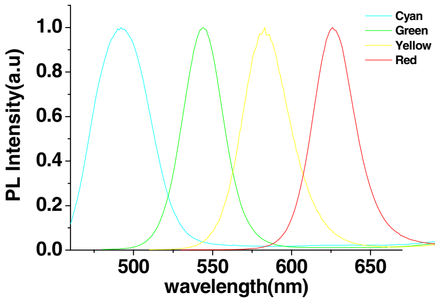


Figure 4. Photoluminescence spectra of our CdSe–ZnS core–shell nanocrystals in UV-curable resin.

as characterized in figure 4. Our blue LEDs have turn-on voltages approximately at 4 V and electroluminescence (EL) peak wavelengths at 440 and 452 nm, as shown in figure 5.

Integrating our blue 440 nm InGaN/GaN LED with single yellow CdSe/ZnS core–shell NCs (with $\lambda_{PL} = 580$ nm), we obtain electroluminescence spectra for different levels of current injection at room temperature, shown in figure 6 along with a picture of the generated white light. Here, to satisfy white light condition, we choose yellow NC for the

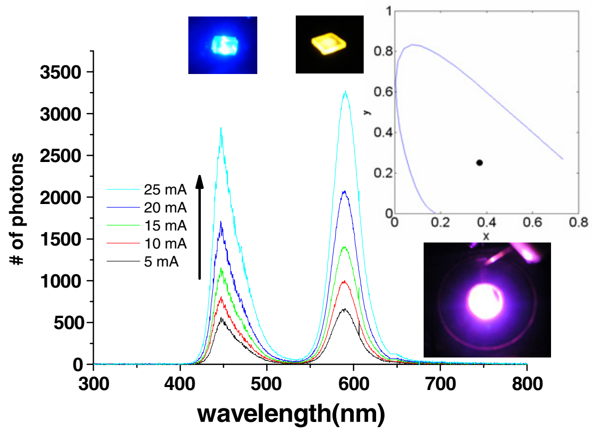


Figure 6. Electroluminescence spectra of yellow NC ($\lambda_{PL} = 580$ nm) hybridized on blue LED ($\lambda_{EL} = 440$ nm) at different levels of current injection at room temperature, along with the corresponding (x, y) coordinates and pictures of the blue LED, yellow NC film and hybrid NC-WLED while generating white light.

hybridization on the blue LED and then design and realize the hybrid NC-LED with its NC film parameters set in accordance with our choice of NC. Consequently, the emission spectra of the resulting hybrid NC-LED experimentally yield tristimulus coordinates of $x = 0.37$ and $y = 0.25$, a correlated colour temperature of $T_c = 2692$ K and a colour rendering index of $R_a = 14.6$. This operating point mathematically falls within the white region of the C.I.E. (1931) chromaticity diagram. However, in this case, the resulting colour rendering index renders low as expected due to the dichromaticity of the hybridization of the yellow NC and the blue LED. Figure 6 also shows the location of the corresponding operating point on the (x, y) coordinates.

Rather than a single type of NC, when we integrate our blue LED ($\lambda_{EL} = 440$ nm) with a dual combination of cyan and

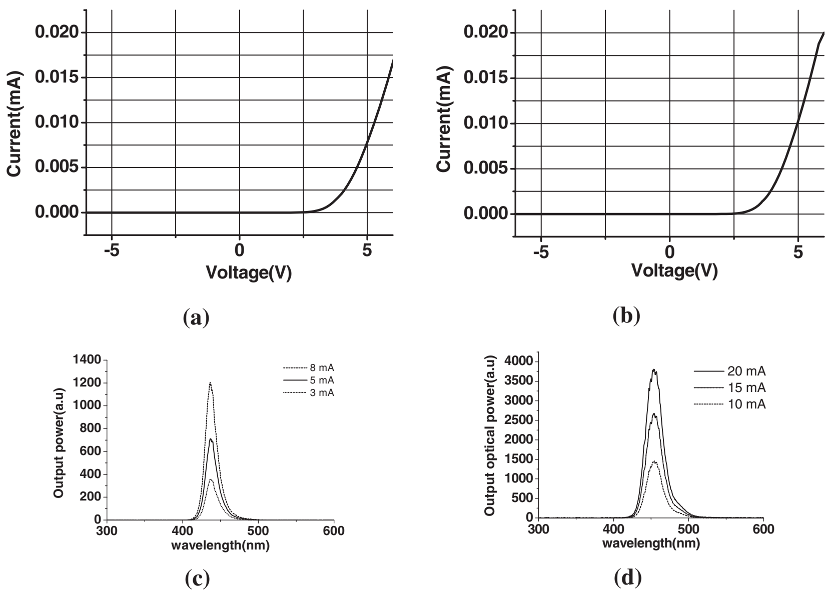


Figure 5. IV characteristics and electroluminescence spectra (at various current injection levels) of the LEDs with emission at 440 and 452 nm: IVs in (a) and (b), and ELs in (c) and (d), respectively.

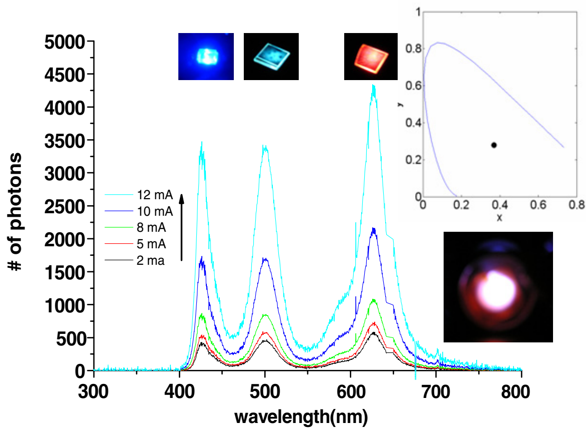


Figure 7. Electroluminescence spectra of a dual combination of cyan ($\lambda_{PL} = 500$ nm) and red ($\lambda_{PL} = 620$ nm) NCs hybridized with blue LED ($\lambda_{EL} = 440$ nm) at various injection current levels at room temperature, along with (x, y) coordinates and pictures of the LED, NC films and hybrid NC-WLED while generating white light.

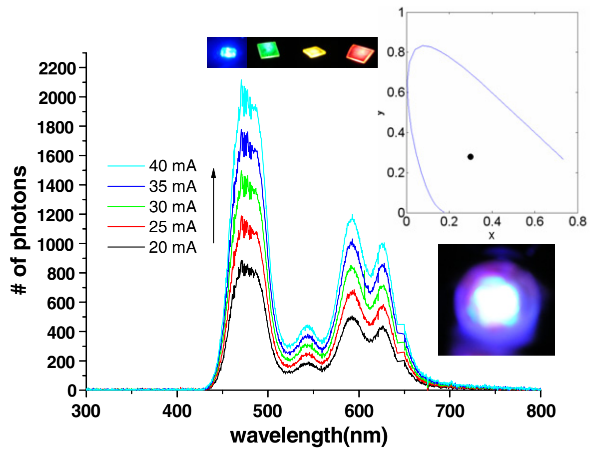


Figure 8. Electroluminescence spectra of a triple combination of green ($\lambda_{PL} = 540$ nm), yellow ($\lambda_{PL} = 580$ nm) and red ($\lambda_{PL} = 620$ nm) NCs with blue LED ($\lambda_{EL} = 452$ nm) at various currents at room temperature, with (x, y) coordinates and pictures of the LED, NC films and hybrid NC-WLED while generating white light.

red CdSe/ZnS NCs ($\lambda_{PL} = 500$ and 620 nm, respectively) with the right device parameters, we obtain electroluminescence spectra at various injection currents at room temperature, as shown in figure 7. Here, we choose the combination of cyan and red NCs so that their contributing photoluminescence mathematically satisfies the white light condition together with the electroluminescence of the integrating LED underneath them. In implementation, we place the red NC layer on the LED and the subsequent cyan NC layer on the red NC layer to minimize re-absorption of the photons emitted from the first NC layer when going through the second adjacent NC layer. In this case, the emission spectra leads to the operating point of $x = 0.37$ and $y = 0.28$, with $T_c = 3246$ K and $R_a = 19.6$. This is also located within the white region of the C.I.E chromaticity diagram, with the corresponding coordinates plotted in figure 7. Here, we observe that the colour rendering index is improved using different NC types and covering larger ranges of the visible spectrum that contribute to white light.

Hybridizing a triple combination of green, yellow and red CdSe/ZnS NCs ($\lambda_{PL} = 540$, 580 and 620 nm, respectively) on our 452 nm blue InGaN/GaN LED, we obtain the electroluminescence spectra presented in figure 8. In this design, we carefully choose the combination of green, yellow and red NCs with the right hybridization parameters to satisfy the white light condition and place these NC films one after the other in the order of longer to shorter PL wavelength to prevent the re-absorption of emitted photons from each NC layer going through the subsequent NC layers. This implementation experimentally leads to $x = 0.30$ and $y = 0.28$ with $T_c = 7521$ K and $R_a = 40.9$, again falling within the white region of the C.I.E. chromaticity diagram shown in figure 8. Here, using a triple combination of NCs, the colour rendering index is further improved.

Finally, combining a quadruple combination of green ($\lambda_{PL} = 540$ nm), cyan ($\lambda_{PL} = 500$ nm), yellow ($\lambda_{PL} = 580$ nm) and red ($\lambda_{PL} = 620$ nm) NCs with the blue LED ($\lambda_{EL} = 452$ nm), we obtain electroluminescence spectra corresponding to $x = 0.24$ and $y = 0.33$, with $T_c = 11\,171$ K and $R_a = 71.0$. This operating point falls in the white region

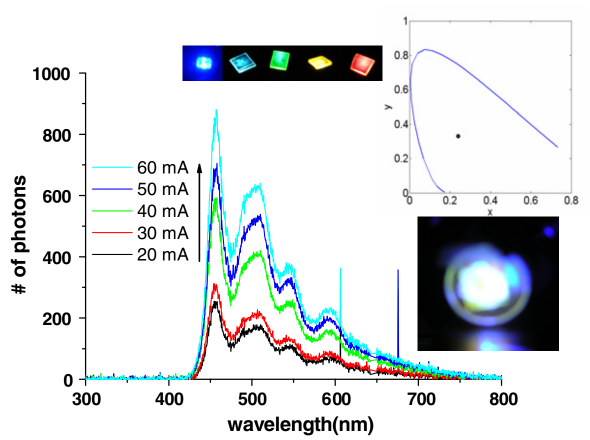


Figure 9. Electroluminescence spectra of quadruple combination of green ($\lambda_{PL} = 540$ nm), cyan ($\lambda_{PL} = 500$ nm), yellow ($\lambda_{PL} = 580$ nm) and red ($\lambda_{PL} = 620$ nm) NCs with blue LED ($\lambda_{EL} = 452$ nm) at various currents at room temperature, along with (x, y) coordinates and pictures of the LED, NC films and hybrid NC-WLED while generating white light.

of the C.I.E. chromaticity diagram like those of the previous hybrid NC-WLEDs. This time, however, the colour rendering index is significantly improved due to the multi-chromaticity of this hybridization based on the combination choice of green, cyan, yellow and red nanocrystals, while maintaining the white light condition. Here the combinations of our nanocrystals limit the maximum achievable colour rendering index in our case, although it is possible to obtain a colour rendering index higher than 90 using the right quadruple combination of nanocrystals in principle. Figure 9 shows the emission spectra at various injection current levels at room temperature, along with the picture of the generated white light.

Hybridizing CdSe/ZnS core–shell NCs of various single, dual, triple and quadruple combinations on our InGaN/GaN

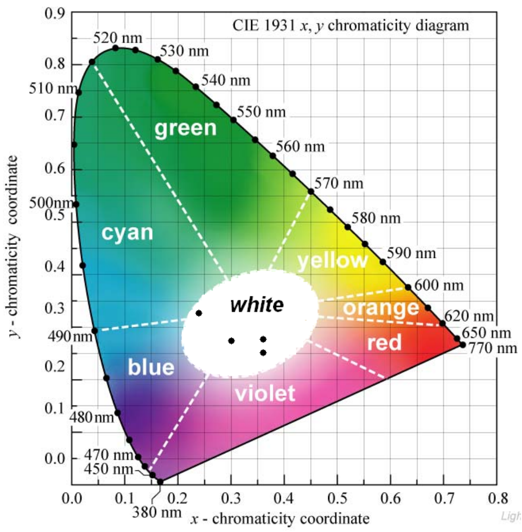


Figure 10. (x, y) coordinates of our white hybrid NC-WLEDs.

based blue LEDs, we demonstrate that the optical properties of the generated white light such as the tristimulus coordinates, colour temperature and colour rendering index are adjusted. Using different NC types in the hybridization with the right hybrid device parameters, the colour rendering index is improved from 14.6 to 71.0. Table 2 provides a list of the hybrid NC-WLEDs presented in this paper, along with the corresponding (x, y) coordinates, colour temperature and colour rendering index. Figure 10 depicts the operating (x, y) coordinates of these four hybrid NC-WLEDs that all fall in the white region of the C.I.E. chromaticity diagram [4].

In conclusion, we introduced CdSe/ZnS core–shell NCs of single, dual, triple and quadruple combinations hybridized with InGaN/GaN LEDs. We presented the design, epitaxial growth, fabrication and characterization of our hybrid NC-WLEDs that are engineered to generate white light with the right device parameters. We adjusted the white light parameters of these hybrid NC-WLEDs such as the tristimulus coordinates, colour temperature and colour rendering index with the NC type and density and the NC film order and thickness. Based on our experimental work, we believe these hybrid white light sources hold promise for future lighting and display applications with their highly adjustable optical properties, and this hybrid approach may be commercially viable with the large-scale synthesis of nanocrystals.

Table 2. Our hybrid NC-WLED sample characteristics.

LED λ_{EL} (nm)	NC λ_{PL} (nm)	(x, y)	T_c (K)	R_a
440	580	(0.37, 0.25)	2 692	14.6
440	500, 620	(0.37, 0.28)	3 246	19.6
452	540, 580, 620	(0.3, 0.28)	7 521	40.9
452	540, 500, 580, 620	(0.24, 0.33)	11 171	71.0

Acknowledgments

This work is supported by a Marie Curie European Reintegration Grant MOON 021391 and the EU-PHOREMOST Network of Excellence 511616 within the 6th European Community Framework Program and TUBITAK under Project Nos 104E114, 106E020, 105E065, and 105E066. HVD and SN also acknowledge additional support from the Turkish Academy of Sciences and TUBITAK.

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